THE PATH TO KRYPTON AND XENON ISOTOPE MEASUREMENTS FROM FEW-MICRON SIZED SAMPLES; I. A LOW-BLANK GAS EXTRACTION SYSTEM.

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A unique noble gas analysis laboratory, previously housed at Atom Sciences [1-2], has been reinstalled at the Institute for Rare Isotope Measurements [3]. The equipment exploits resonance ionization, an emerging laser-based element analysis technique. This technique efficiently measures minute quantities of a particular element in the presence of an overwhelmingly larger background of other material [1]. The system is being upgraded to provide routine noble gas measurements from few-micron sized terrestrial and extraterrestrial samples.

Resonance Ionization Spectroscopy Time-of-Flight mass spectrometry (RIS-TOF) utilizes lasers tuned to specific atomic energy levels of the analyte element, thus producing only ions of the chosen element. The ionization efficiency is higher than that of conventional methods such as electron bombardment, thermal ionization, or ion sputtering. Coupling this efficiency with the absence of interfering ions from the other, usually major, sample constituents, leads to significant improvements in detection limits. A static noble gas RIS-TOF system utilizing a cryogenic sample concentration has demonstrated a detection limit of ~ 100 ^{85}Kr atoms [2]. This results in an extremely fast analyzer of ~ 3 min. detection half-life vs. ~ 60 min. for conventional systems. The short analysis time reduces the background contribution of outgassing in the mass spectrometer, which is one of the most important performance parameters for a low-level noble gas analyzer. A similar system, designed exclusively for Xe analyses, has been constructed at Manchester University [4].

The RIS-TOF consist of four major components: (1) a cryogenic sample concentrator, (2) tunable laser(s) to promote the valence electron through one or more excited states to ionization, (3) a filter to separate the different ion masses, primarily isotopes, and reject interfering ions, and (4) an ion detection and data collection system. This system employs pulsed atomization and ionization to optimize sample utilization efficiency and element accessibility.

Recent studies have focused on the separation of highly refractory microscopic grains from the much more abundant carbonaceous matrix in primitive meteorites [5]. They have shown a remarkable isotopic composition diversity in a small fraction of single grains from the same meteorite, inferring multiple stellar sources [6]. The University of Chicago group led by Lewis, has isolated a large number of refractory grains in primitive meteorites and has published a number of comprehensive studies of the noble gas and isotropic abundances in SiC, graphite and diamonds [7-12]. Pursuing similar studies of noble gases from primitive meteorites is Hohenberg and his colleagues at Washington University [13-14]. The Washington group has extended the work to Ne from individual olivine grains, Ne and ^{4}He from single SiC and Ca grains, He, Ne and Ar from single lunar ilmenite grains and Xe from individual phosphate grains [1-18]. The unique advantage of grain-specific isotope data and a recent unsuccessful attempt to measure the noble gases from individual "X" SiC grains with the ~ 2000 ^{132}Xe atom detection limit of conventional mass spectrometer have made this field ideal for the RIS-TOF.

The RIS-TOF has been equipped with a new extraction chamber that is designed to hold thin sections or multiple individual grains of the study sample. Special emphasis in the design and construction was directed towards lowering outgassing and minimizing volume. All welds

of the components in the static-vacuum sections of the system were made with He shielding gas, rather than Ar, and the internal surfaces were mechanically polished. All other components were electropolished. The sample holder itself resides in the vacuum system behind a sapphire viewport. Through this the 4^{th} harmonic (266 nm) of a pulsed Nd:YAG laser can be focused to a diameter ranging from 2 mm to ~4 μm to vaporize selected individual grains. The entire sample chamber is mounted on a precision X/Y translation stage having 2 μm resolution and +/- 25 mm travel in each direction. The thin section will be mapped visually, identifying mineral grains to be analyzed before being placed into the chamber. An optical microscope collinear with the laser beam, will be used to align the desired mineral for vaporization. If necessary, the gases liberated can be purified by brief exposure to various getters, but the ionization specificity of the RIS-TOF may make it feasible to release the gas directly into the system for analysis.

Several improvements are being implemented to enhance the RIS-TOF performance. A wide-range turbomolecular vacuum pump has been installed to reduce the base pressure and permit baking of the ion pumps. To further aid in the reduction of the background, copper gaskets were replaced with silver plated gaskets to maintain tighter seals. Furthermore, much of the system's plumbing was reconfigured to enable baking of the entire system at 250° to 300°C (previously, only parts of the system had been baked). A new gas standard inlet system has been designed and added to the RIS-TOF. This standard inlet system introduces only 10^4 to 10^5 Kr and Xe atoms, and eliminates uncertainties due to the scattering that was noted from the previous $1{:}10^5$ Kr:Ar mixture calibration technique. A new Nd:YAG pump laser and dye laser will be added to enable simultaneous Kr and Xe analyses.

Calibration of the RIS-TOF will initially use the new gas standard inlet system. Detail studies will be taken in determining the reproducibility and stability of the laser system to permit accurate isotope ratio measurements, and to reliably subtract background measurements. Next, the micron size sample extraction technique will be tested by using a relative homogenized terrestrial sample. Three subsets of the whole rock will be made. One subset will be analyzed by standard step-wise heating at Washington University on a conventional noble gas mass spectrometer. A second whole rock subset will be finely crushed and further homogenized. This subset will be made into pellets for laser vaporization using a wider beam, permitting the gas to be analyzed by the RIS-TOF. The third subset will be a thin section of the terrestrial sample. Individual mineral phases will be vaporized, thus providing grain specific Kr data. These analyses will give a basis to compare Kr isotope measurements (and later also Xe) for the RIS-TOF system with conventional static noble gas mass spectrometry.

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